Qualitative Composition Analysis

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Qualitative analysis does not give you a composition down to the particular parts count, but it will allow you to determine all the chemicals involved. Generally that is sufficient, but if you wish to duplicate the composition then common sense and careful quantitative analysis of each component can be used to completely reverse engineer the composition.

Generally we start by making some assumptions. We often know the purpose of the composition from where it was found. We look at the loose composition, what parts can we identify visually or by smell. A microscope is very handy to observe the particle sizes and many materials can be identified by appearance alone, in particular Sulfur, Charcoal, Gums, Shellac, Magnalium, etc.

We test burn some on a white tile outside and observe its properties, the colour of the smoke and ash. Colour compositions are immediately obvious. The particular species involved will guide assumptions about the oxidiser or colour donor to look for. Flash or other report compositions will be obvious by their burn rate. The colour of the residue is generally a big hint at the oxidiser, bluish powdery material suggests a chlorate or perchlorate over a nitrate, as will the smell of the smoke. The sparks will tell you a lot about the metals present.

Many qualitative chemical tests require an aqueous solution. This is prepared by placing some solid composition in a dry test tube and adding distilled water. The tube is warmed gently and any changes observed. A gentle boil is useful to get less soluble material into solution. Fine Aluminium may form a mirror on the surface, denser and coarse metals will just tend to sink. A centrifuge is very handy in settling out insolubles, but a filter or gravity will work.

Once chlorate is ruled out as the major oxidiser acid solutions are often used, either HCl or H2SO4. They are prepared in much the same manner as those made with distilled water. Gas production is to be expected and allowed for. Lye is handy for dissolving Aluminium and many organics or greasy materials. Potassium salts of particular reagent species are useful if you do not wish to upset colours in flame tests.

It is quite useful to separate out the components into:

- "water soluble" - oxidisers, etc
- "acid soluble" - most metals, Carbonates, Oxides and Sulfides
- "alkali soluble" - fats and Aluminium
- "alcohol soluble" - gums and resins
- "ketone soluble" - resins and polymers
- "carbon disulfide soluble" - Sulfur, chloroprene
- "insolubles" - Titanium, Charcoal, inert material.

Oxidiser

The oxidiser will generally be a Chlorate, Perchlorate, Nitrate or mixture of the three. Remove the possibility of a chlorate first as it drives your treatment of the composition. Nitrate and Perchlorate mixtures are common and annoying to separate.

Chlorate

- Prepare a boiling solution of 5 parts strong HCl and 1 part aqueous 0.1 % Indigo Carmine. Add 5-6 parts of the dissolved composition to the boiling reagent, a sharp de-colourisation is indicative of Chlorate. This test is very sensitive.
- Place a small quantity of composition in a white well plate and cover with several drops of Aniline Hydrogen Chloride. A blue or green colouration forming within half an hour is indicative of Chlorate. This test has reasonable sensitivity.
- Place a small quantity of composition on a tile outside and cautiously touch a stirring rod dampened with concentrated Sulfuric Acid to it. Ignition indicates Chlorate. This test is not considered reliable or safe.

Perchlorate

- Add a few drops of 0.3% aqueous Methylene Blue solution to an aqueous solution of the composition. A purple precipitant is indicative of Perchlorate. If a purple colouration is produced raise pH with strong NaOH or KOH as the precipitant will only form at high pH. Nitrates will form a blue precipitant rather than a purple one. This test is quite sensitive.

Nitrate

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- Eliminate Chlorate and Perchlorate and there is a very good chance Nitrate is the only oxidiser. A blue precipitant with 0.3% aqueous Methylene Blue is fairly indicative.
- Brown-Ring test - take a clear acid dissolved sample and saturate with Iron Sulfate, cautiously run concentrated Sulfuric Acid down the side of the test tube it will sink to the bottom. A violet-brown ring will form at the interface in a few moments if Nitrate is present. Heavy metals can confuse this test, precipitate them out with a Carbonate first to disambiguate.

Lithium, Sodium, Potassium, Calcium, Strontium, Barium

Strontium should be immediately obvious from the colour the composition burns or in a flame test. It is generally too expensive and hygroscopic to bother using in a composition unless it is there as a colour donor.

Calcium can be a bit difficult to separate from Strontium and Sodium, but the colour is distinct.

Stontium, Barium and Calcium can be precipitated as the Carbonate or Sulfate by the addition or Potassium or Sodium Carbonate or Sulfate solutions. Potassium or Sodium will of course not precipitate. Sodium can be shown by its colour in a flame test.

The Potassium purple is generally hard to observe unless there is little else in the composition. Lithium is rare in compositions, except maybe in exotic rocket propellants and Oxygen candles as the Perchlorate. Its beautiful lilac-red colour is very distinctive in a flame test, but generally not visible in the burning composition. Your chances of running across Beryllium, Caesium or Rubidium is very low unless you work with exotic military stuff.

Indium might become a rare find in the future, it is quite plentiful - similar to silver, but still very expensive at this time.

Metal Fuels

Metals can be extracted from the water insoluble fraction.

Iron and most of its alloys are ferromagnetic and can be isolated with a magnet. The blood-red colouration of the Thiocyanate is indicative. It is generally precipitated from a Nitric Acid solution (to oxidise it to Fe+++) with Ammonium Thiocyanate.

Magnesium and Zinc will dissolve easily into Hydrochloric acid, their reactivity difference is obvious. Zinc forms an insoluble Sulfide from an Ammonia complex by adding a little Sodium Sulfide.

Aluminium can be dissolved in strong Lye solution. Aluminon is a specific test for the Aluminium ion but it is often easier to just eliminate everything else.

The Hydrogen produced by dissolving metals in general can be "popped" in a test tube, but this test is considered dangerous and is now depreciated.

The physical form of the metal can be observed visually, a microscope helps with smaller particles. If large enough quantities are available a particle size breakdown can be made with a sieve stack.

Titanium can be determined by its extreme inertness to most reagents. Its wonderful white sparks in air are similar only to Zirconium.

Magnalium's relatively low reactivity compared to Magnesium and its physically brittle nature helps its identification. The sizzling sound of its burning is also characteristic.

Inert coating on metals can hamper their dissolving. Gentle warming will generally get the process started. A wash in strong Lye will break down most barrier coatings. Chromate treatments however do pose a bit of a problem, hot acid will work.

Copper, Arsenic, Antimony, Lead, Bismuth, Mercury

Copper will be seen by its colour in a burn test, but will be green with blue tinged edges when tested in a bunsen flame rather than burnt in the composition. The blue/green solution colour can also be observed in the acid solution if sufficiently strong. The behaviour of the Carbonate and Hydroxide are difficult to mistake. Eliminating Paris Green as the copper source can be done by testing for Arsenic using the Reinsch test. Unfortunately it is also sensitive to Bismuth, Antimony and most other heavy metals.

Essentially you place Copper metal just cleaned with Nitric Acid into a filtered concentrated Hydrochloric Acid solution of the composition and boil for one hour. A black deposit on the Copper is indicative. The exact nature of the deposit can be read to determine the heavy metal involved, but this is a difficult skill and requires controls to be produced for comparison. The test is quite sensitive.

Bismuth Hydroxide precipitate can be reduced to black elemental Bismuth by a Tin Hydroxide solution. This is a very specific test for Bismuth.

The canary-yellow Lead Chromate is a fairly specific test for Lead. It is best precipitated from the Acetate solution which is generally prepared by precipitating the Chloride or Sulfate and dissolving it again in Acetic acid. The whole process confirming the presence of Lead.

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Boron is often present as Boric Acid used with Aluminium as an buffer, but may also be found rarely as Borax as a yellow colour donor, cooling or glitter delay agent, and rarely amorphous Boron can be found in some (primarily military) compositions.

For the amateur Boron detection is probably going to be difficult. However I've had success with Curcumin paper. Turmeric was extracted with Methanol and filtered. The powerful dye was painted onto filter paper and allowed to dry. On this paper a drop of the acidified solution is placed, a slight orange colouration may be seen if boron is present. After drying a drop of Carbonate or Hydroxide solution is used to raise the pH, a blue colouration where the previous drop was is indicative of Boron. Pure reagent grade Curcumin is best, but the mixture of Curcuminoids extracted from quality Turmeric will work.

Ammonia

Detected by smell from a boiling alkaline solution. Fuming with HCl is a common test that saves the nose. Be careful that you are not observing the product of a Nitrate/Metal reaction.

Sulfur and Sulfides

Elemental Sulfur is easily detected by its microscopic appearance and distinctive smell. It can be dissolved out fairly selectively using Carbon Disulfide for quantitative analysis, but note that chloroprene is also soluble to some degree if it is also present.

If Hydrochloric Acid is added to the composition and boiled Hydrogen Sulfide will be released if a Sulfide or elemental Sulfur is present. The smell is unmistakable, however dampened Lead Acetate paper is the traditional indicator - it will darken in the presence of Hydrogen Sulfide. The human sense of smell for Hydrogen Sulfide is quickly desensitised so the indicator paper is handy for a batch of tests, but not really required for a one-off essay.

The particular sulfide is determined by characterising the metal ion in solution as in the Reinsch test or by its characteristic colour. Iron is the most likely Sulfide other than Antimony or Arsenic. Iron's deep-black complex with Tannic Acid may be a easier test for amateurs than the traditional Thiocyanate one. The specific type of Sulfide can be determined visually if enough is available particularly for Arsenic.

Sulfates

Sulfates are easily precipitated as the very insoluble Barium Sulfate using a few drops of Barium Chloride solution. This is done from an strongly acid solution to prevent other insoluble Barium compounds being mistook for the Sulfate.

Carbonates

The Carbon Dioxide formed when acid is added to the composition can be detected by bubbling through a freshly prepared saturated Calcium or Barium Hydroxide solution.

Bicarbonates will react in a similar manner.

Chromates

Chromium has many coloured compounds making it quite easy to test for exhaustively. However the trivalent green precipitate with Hydroxide and hexavalent orange oxidised with Nitric Acid or Potassium Permanganate are generally sufficient.

Manganese

Oxidation of Manganese to the purple Permanganate using Sodium Bismuthate is the usual test but is somewhat exotic, sensitive to impurities and difficult to carry out.

Charcoal, Lampblack and Graphite

Charcoals are easily detected by their appearance. Both are essentially completely inert in all solvents. Charcoal will de-colourise most food dyes in a weak aqueous solution, graphite or lampblack will not. Microscopic examination allows the type of timber used to be determined with quite good accuracy.

Lampblack will tend to float on water and blacken paper that the composition is placed on. Its amorphous nature is easily distinguished from charcoal. It burns with much difficulty.

Graphite is greasy and electrically conductive. Lampblack may be similar, but the lustre of graphite is not present with lampblack. Graphite is almost impossible to burn.

Redgum and Shellac

Easily dissolved out by warm alcohol and separated. The colour and physical appearance can be used to distinguish between Shellac and Redgum. Redgum often has a sweet smell, while shellac an earthy one, if any at all.

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Insoluble in water and alcohol. Parlon and PVC are soluble in ketones to some degree, more so in Xylene. Mixtures of MEK and Xylene can dissolve most Chlorine donors except perhaps Saran.

Chlorine content visible by burning on copper wire to give blue colour. Halide-free polymers will not enhance the copper flame colour.

Chlorides

Precipitate with Silver Nitrate solution from the aqueous soluble fraction.

Starch

The blue-black complex with elemental Iodine is a simple test.

Sugars

Easily water soluble, the aqueous fraction may be somewhat yellow especially for dextrin and modified cellulose.

Molisch's and Bial's tests are ideal as they will detect just about all carbohydrates. However the reagents are harder to get and work with than those for Benedict's or Fehling's tests.

Benedict's or Fehling's tests are simple and quick, but are also limited to reducing monosaccharides. Prolonged boiling of sucrose solutions will generally cause a reaction due to hydrolysis to dextrose but lactose will react directly with Benedict's on heating.

Nitrocellulose

Soluble slowly in acetone. Forms a thin flexible sheet on drying in a watchglass which burns with a large smokeless yellow flame.

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